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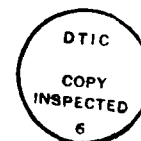
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ordering of the molecular structure as the film thickness is reduced below 200 nm; this increase is most marked for materials of large molecular weights. This suggested that the lithographic properties and the defect (pinhole) density of such films might be significantly different from the results expected by extrapolation from thicker (>200 nm) films. Ultrathin poly(methylmethacrylate) (PMMA) films (thinner than 20 nm) prepared by LB and spin-cast techniques and novolac resists prepared by the spin-cast technique were explored as electron beam resists, using a Perkin Elmer MEBES I pattern generation system for exposure. The results have demonstrated the resolution and etch resistance capabilities of such films for patterning 100 nm features in 50 nm of chromium film. The most surprising result has been that the pinhole density in these films has been far lower than previously expected levels.



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Studies of Ultrathin Polymer Films for Lithographic Applications

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ABSTRACT

The advantages of minimizing polymer resist thickness to the macromolecular dimensions are manifold. In optical lithography, ultrathin resists can improve exposure and focus latitude and alleviate the problem of absorption in conventional resists for deep ultraviolet (UV) exposure. In electron beam lithography it is desirable to reduce the resist thickness to minimize forward electron scattering in the resist, and to allow penetration when using the scanning tunneling microscope (STM) as a very low voltage exposure source. Moreover, we can better understand many phenomena such as the nature of the pinholes and etching resistance, which are still puzzles for the thicker films. Here we describe the preparation and characterization of resists of ultrathin polymer films (10 nm to 200 nm) formed by both the Langmuir-Blodgett (LB) and spin-cast techniques. The characterization techniques include fluorescence spectroscopy, electron beam exposure and development, and etch resistance. The fluorescence spectroscopy results of spin cast polystyrene films suggest a dramatic increase in the ordering of the molecular structure as the film thickness is reduced below 0.2 μm ; this increase is most marked for materials of large molecular weights. This suggested that the lithographic properties and the defect (pinhole) density of such films might be significantly different from the results expected by extrapolation from thicker (>200 nm) films. Ultrathin poly(methylmethacrylate) (PMMA) films (thinner than 20 nm) prepared by LB and spin-cast techniques and novolac resists prepared by the spin-cast technique were explored as electron beam resists, using a Perkin Elmer MEBES I pattern generation system for exposure. The results have demonstrated the resolution and etch resistance capabilities of such films for patterning 0.1 μm features in 50 nm of chromium film. The most surprising result has been that the pinhole density in these films has been far lower than previously expected levels.

1. INTRODUCTION

The importance of polymer films in microelectronics technology is perhaps greatest in the area of resist materials for lithography. In photolithography, present day minimum feature sizes in manufacturing are between 1 and 2 μm . Ten years hence minimum feature sizes should be 0.5 μm or less. Manufacturing VLSI circuits with 0.5 μm feature sizes requires feature size control of 50 nm and defect densities less than 1/cm². Present day resist thicknesses have a minimum value of about 0.5 μm to minimize the occurrence of defects, but achieving adequate linewidth control in such thick films is proving difficult even at today's feature sizes. In order to have a better control of the linewidth for photolithography, the idea of ultrathin resist films (20 - 200 nm) has been proposed. There are several other advantages of using the ultrathin resists. In deep UV lithography, ultrathin resists can reduce the problem of absorption by the resist matrix. In conventional electron beam lithography, ultrathin resists can reduce the electron scattering within the resist films. Moreover, ultrathin resists can open up a new lithography area using STM as the exposure tool¹. Because the STM is capable of creating patterns with extremely high resolution (less than 10 nm) and potentially at very high speed, it may become an important lithography tool in the near future. Despite these advantages, however, little work² has been reported in the area of ultrathin resists. In this paper we have investigated the preparation techniques and characterized the lithographic properties of such resist films.

Two techniques have been used to prepare the ultrathin resist films. The first method is spin-casting, which has been used for preparation of thick resists for the last two decades. The thickness of the spin-cast film depends on many parameters such as spinning speed, solution concentration and polymer molecular weight. In order to prepare ultrathin resists, dilute solutions and high spinning speed (>5,000 rpm) have been used. The second method we used is the Langmuir-Blodgett (LB) technique³, with which polymer films can be transferred to the substrate layer by layer from the water surface as the substrate is dipped into or pulled out from the water subphase. Both methods offer the possibility of depositing ultrathin films with very good thickness uniformity. Spin-cast and LB poly(methylmethacrylate) (PMMA) films and spin-cast novolac films with thicknesses less than 20 nm were exposed with MEBES, and an underlying chromium film was etched following resist development. The resulting patterns allowed evaluation of these resist films in such applications as high-resolution mask making.

In order to understand the microstructure of the ultrathin resist films and how this microstructure relates to macroscopic properties such as sensitivity, contrast, etch resistance and susceptibility of lithographic defects, fluorescence spectroscopy has proved to be a very promising technique. We have used fluorescence to investigate the polymer configurational changes induced by the spin casting. Intrinsic fluorescence can be used as a very sensitive probe of the polymer environment and configuration. A particular example is excimer fluorescence, which can occur when two aromatic groups interact in a coplanar structure. The rings must be within three to four angstroms to produce a suitable excimer forming site, so the excimer fluorescence yields information on the local concentration of aromatic chromophores. Excimer formation may be intermolecular if the two aromatic rings are on different polymer chains, or intramolecular if they are on repeating units of the same polymer chain. Changes in the ratio of excimer to monomer fluorescence intensity of aromatic polymers such as polystyrene can be used to study the chain orientation induced by spin casting. We have been applying this technique to study resist films spin cast under different conditions and have discovered striking changes in the fluorescence as the resist thickness is reduced to 0.2 μm and below.

2. EXPERIMENTAL

2.1. Samples for fluorescence spectroscopy measurements

Polystyrene samples with molecular weights 50,000 and 600,000, both with narrow molecular weight distributions ($M_w/M_n < 1.1$, where M_w is the weight average molecular weight and M_n is the number average molecular weight) were obtained from Polysciences Inc. They were purified by three consecutive precipitations from tetrahydrofuran (THF) into methanol. Spin-cast films of polystyrene (0.1 μm - 1 μm) for fluorescence spectroscopy measurements were prepared by dropping dioxane solution onto quartz wafers and then spinning them in a dry nitrogen ambient at a given spin speed for 60 seconds using a Metron System Inc. LS-8000 spinner. A dry nitrogen ambient is required to reduce the uptake of moisture by the dioxane, which can lead to poor film quality.

2.2. Samples for electron-beam exposure experiments

Two different resists have been used. For PMMA both spin-cast and LB methods have been employed. For novolac only the spin-cast method has been applicable. The PMMA sample with a molecular weight of 188,100 and $M_w/M_n < 1.08$ was purchased from Pressure Chemical Company without further purification. The spin-cast PMMA films with a thickness of 14 nm (measured by ellipsometry) were prepared by spinning 7.5 mg/ml chlorobenzene solution at 8,000 rpm for 30 seconds. The LB PMMA films with a thickness of 15.3 nm were deposited with a Joyce-Loebl IV trough. After spreading 2 ml of 0.5 mg/ml chloroform solution on the water subphase, several compression and expansion cycles were performed until the pressure-area isotherm became reversible. During the film transfer the pressure was fixed at 15 dyne/cm, since PMMS can form a monolayer on the water surface at this pressure. The first monolayer of PMMA was transferred to the substrate by pulling the substrate, that had been immersed in the water before spreading the chloroform solution, out of the water. After the substrate was completely pulled out of the water, it was baked at 100°C for half an hour to improve the adhesion of the first monolayer to the substrate. Eight continuous cycles of dipping in and pulling out of the water subphase were then performed. The thickness of the LB PMMA films after 17 layers of PMMA were transferred was 15.3 nm, corresponding to 0.9 nm per monolayer. Both spin cast and LB PMMA films were prebaked at 170°C for 8 hours before exposure experiment.

The novolac sample we used in this study was diluted AZ 5206 resist. In particular, by spinning AZ 5206 diluted 1:10 at 5,000 rpm, a film thickness of about 22 nm was obtained. The novolac sample was prebaked at 90°C.

The substrates used in these experiments were 50 nm evaporated Cr films over 100 nm thermally grown silicon dioxide on silicon wafers. The Cr and oxide layers provide an excellent contrast for evaluating etched Cr patterns with both optical and scanning electron microscopes (SEM).

2.3. Fluorescence instrumentation and measurements

Fluorescence spectra of the PS samples were obtained on a steady state spectrofluorometer of modular construction with a 1000 W xenon arc lamp and tandem quarter meter excitation monochromator and quarter meter analysis monochromator. Uncorrected spectra were taken under front-face illumination with exciting light at 260 nm. Monomer fluorescence was measured at 280 nm and excimer fluorescence was measured at 330 nm.

3. RESULTS AND DISCUSSION

3.1. Fluorescence of Polystyrene Films

Polystyrene films of various molecular weight polystyrene were prepared at spin speeds ranging from 1,000 to 8,000 rpm. The ratio of excimer to monomer emission intensities, I_e/I_m , as a function of the film thickness is shown in Table 1a and Table 1b for molecular weight of 600,000 and 50,000, respectively.

Table 1a

I_e/I_m of 600,000 Molecular Weight Polystyrene
at different thicknesses

I_e/I_m	11.42	13.46	14.65	16.56	17.15
Thickness (nm)	304.1	210.9	150.2	122.6	104.2

Table 1b

I_e/I_m of 50,000 Molecular Weight Polystyrene
at different thicknesses

I_e/I_m	10.16	11	11.53	11.65	12.08
Thickness (nm)	519.6	363.9	260	211.1	180.7

I_e/I_m values are strongly dependent on the film thickness, increasing as the film thickness decreases. These results suggest that the polymer chains become oriented parallel to the substrate as they are closer to the substrate, leading to either an increasing in the chance to form an excimer forming site or an increasing in the energy migration rate among the aromatic rings. This could explain the higher I_e/I_m values.

3.2. E-beam exposure experiments

Spin casting and LB PMMA films with thicknesses of 14 and 15.3 nm, respectively, and spin cast novolac film with a thickness of 22 nm were exposed with a modified Perkin Elmer MEBES I pattern generation system. The MEBES exposures were performed at 20 MHz address rate, 10 kV accelerating voltage, 1/8 μ m spot diameter, and 6 nA spot current giving a dose of 2 μ C/cm² per pass. Equal line-space patterns with feature size down to 1/8 μ m were written. The dose ranges for this study were 1 - 200 μ C/cm² for PMMA and 1-20 μ C/cm² for novolac resist. Only positive resist actions have been observed in these ranges. PMMA was developed in a solvent made of 3:7 cellosolve - methanol; cellosolve is chosen because it is strong enough to dissolve PMMA molecule fragments but not the original high molecular weight PMMA itself. For novolac, KLK PPD-401 developer diluted 1:1 with deionized water was used as a developer. Postbaking at 90°C for half an hour was performed after developing. Following the postbaking process the samples were put in a Cr etching solution (Cr-14) for 30 seconds to transfer the pattern from resist to Cr. Figure 1 shows the patterns in Cr film with a 14 nm spin cast PMMA film as a positive resist. Figure 2 shows the patterns in Cr with a 15.3 nm LB PMMA film as a positive resist. Figure 3 shows the patterns in Cr with a 22 nm novolac film as a positive resist.

The pinhole densities estimated with optical microscopy are less than 1 pinhole per cm² for the 100 nm novolac resist, 8 pinholes per cm² for the 22 nm novolac resist, 5 pinholes per cm² for the 15.2 nm LB PMMA resist and about 10⁴ pinholes per cm² for the 14 nm spin cast PMMA resist. The drastic difference in the pinhole density among the three different types of film are still under study.

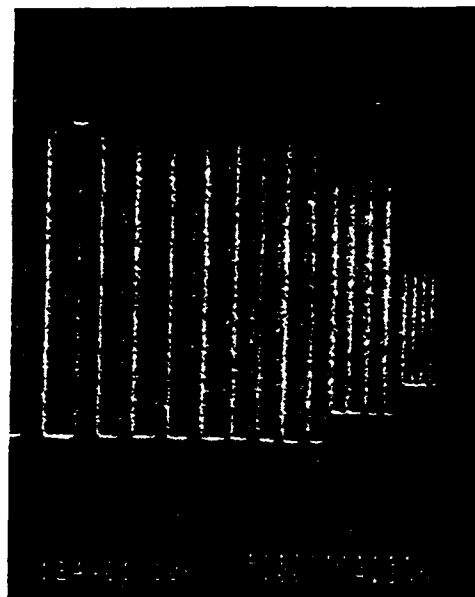


Figure 1. Features in 50 nm Cr film patterned with 14 nm spin-cast PMMA resist, exposed on MEBES at 10 kV and a dose of 200 $\mu\text{C}/\text{cm}^2$.

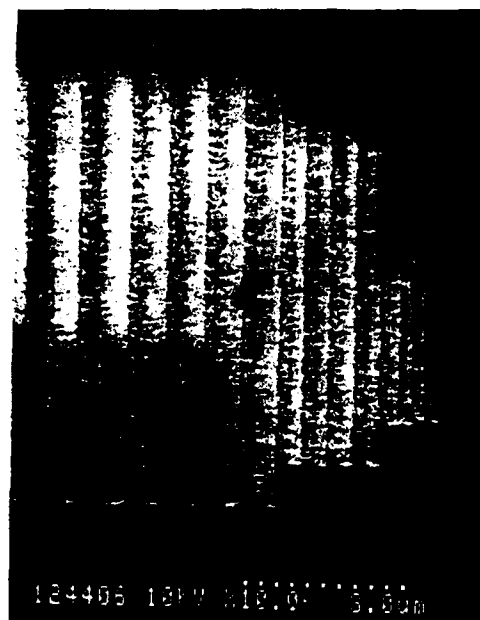


Figure 2. Features in 50 nm Cr film patterned with 15.3 nm LB PMMA film, exposed on MEBES at 10 kV and a dose of 200 $\mu\text{C}/\text{cm}^2$.

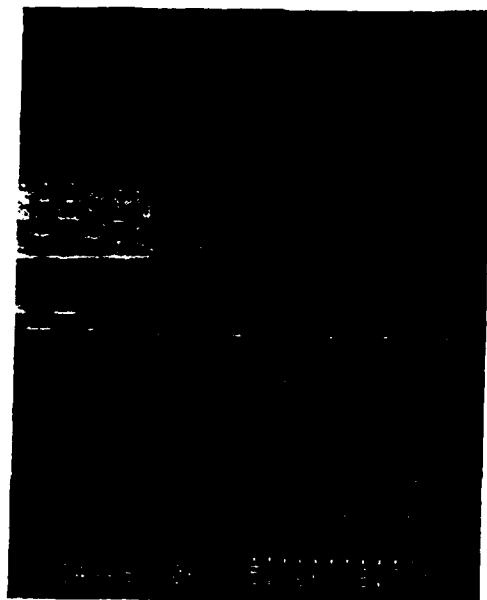


Figure 3. Features in 50 nm Cr film patterned with 22 nm novolac resist, exposed on MEBES at 10 kV and a dose of 10 $\mu\text{C}/\text{cm}^2$.

4. CONCLUSIONS

We have investigated the lithographic properties of ultrathin spin-cast PMMA film (14 nm), LB PMMA film (15.3 nm) and spin-cast novolac film (22 nm) as resists. We demonstrated that the ultrathin resists have potential for high resolution lithography in the nanometer regime. The fact that can achieve only a few pinholes per cm^2 at a thickness fifty times less than that used today suggests that we should seriously consider the use of much thinner imaging layers than has been common practice. We also demonstrated that the fluorescence technique is a very sensitive tool to study the film structure at a microscopic level. A better understanding of the film structure can help us to design new resist materials and even to modify conventional resists for nanolithography.

5. ACKNOWLEDGEMENTS

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